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# Indirect Oxidation of $LiCoO_2$ Electrodes: More Severe Conditions to Analyze the Interface Performance

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The transport of electrolyte was characterized by the probe current above the $LiCoO_2$ substrate using the probe approach curve (PAC) at a constant probe potential (4.8 V) and linear sweep voltammetry (LSV) at a fixed position from the substrate. The current in the LSV experiment increased as the probe was within 3 μm of the substrate, whereas the current at the PAC decreased significantly. The increase of the probe current in the LSV was induced by the circulation of the redox reactant, $PF_6^-$ ions, which is continuously oxidized at the probe while the oxidized species is reduced at the $LiCoO_2$ substrate in the narrow space. This indirect oxidation of the $LiCoO_2$ substrate was observed by applying the Probe Generation/Substrate Generation to the Probe Collection (PG/SG→PC) mode, which is more severe than the typical SG/PC mode. Therefore, this approach provides new technology to design an electrolyte for Li ion batteries with high rate performance.

**Keywords:** electrolyte transport, feedback current, redox reaction of $PF_6^-$ ion, indirect oxidation, PG/SG→PC mode.

## 1. INTRODUCTION

Recently, Li ion batteries have been used in electric vehicles (EV) and hybrid electric vehicles (HEV) which require both high capacity and high power [1, 2]. To comply with these demands, many researchers have focused on the development of new active materials and electrolyte components [3]. Moreover, to maximize the performance of these materials, some studies have focused on the diffusion of $Li^+$ ions within the active materials, the transfer of $Li^+$ ions at the electrode interface, and the transport of $Li^+$ ions in the electrolyte [4]. Many instruments including a scanning electron microscope (SEM), a transmission electron microscope (TEM), an atomic force microscope (AFM), and X-ray diffraction (XRD) have been used to investigate these electrochemical reactions [5-7]. However, these instruments only make full use of their observation capabilities after the electrochemical reaction on the electrode is completed. Therefore, other appropriate tools are needed to investigate the *in situ* interfacial reaction. A scanning electrochemical microscope (SECM) is very useful for this purpose because it can utilize a probe as either a detector or a generator of the electrochemical reaction above the substrate [8]. This work presented herein describes the electrolyte transport above the $LiCoO_2$ substrate through the redox reaction of $PF_6^-$ ions using the probe approach curve (PAC) and the linear sweep voltammetry (LSV) of the SECM. In these experiments, $PF_6^-$ ions are oxidized at the probe and the oxidized form, $PF_6^0$, diffuses to near the $LiCoO_2$ substrate. The $PF_6^0$ is reduced by the $LiCoO_2$ substrate and $Li^+$ ions are dissociated from the substrate simultaneously. Finally, these circular behaviors affect the oxidation of $PF_6^-$ ions at the probe as a stronger current. Although this circular reaction is similar to the typical feedback mode of the SECM, the probe generation/substrate collection (PG/SC) [9], it can be referred to as probe generation/substrate generation and probe correction (PG/SG→PC) because the PC is affected continuously by the oxidation of $PF_6^-$ ions (PG), the reduction of $PF_6^0$ (SG), and the deintercalation of $Li^+$ ions from the substrate (SG). That is, the $LiCoO_2$ substrate is oxidized indirectly by this PG/SG→PC process, which is more severe than the direct oxidation process of the $LiCoO_2$ substrate, which is the typical SG/PC mode in SECM experiments.

By applying this research method, we analyzed $Li^+$ ions dissociating from a $LiMO_2$ electrode from a new viewpoint, considering the electrolyte and electrode. In addition, these experimental tools can be applied to the intercalation of $Li^+$ ions into a graphite electrode with the same mechanism if a Li probe is used instead of a Pt probe. Therefore, this method could serve as a promising tool to analyze the interface performance of high power Li ion batteries.

## 2. EXPERIMENT

The electrolyte comprised of a 3:7 volume ratio of ethylene carbonate (EC) and diethyl carbonate (DEC) in 1.0 M $LiPF_6$ was received from Techno Semichem Co. The substrate coated with $LiCoO_2$ was received from Enerland Co. and is the grade used for the mass production of Li ion batteries. The electrochemical measurements to obtain the results of linear sweep voltammetry (LSV) and probe approach curves (PAC) were carried out using a SECM (CHI900B) installed in an Ar filled glove box (MBraun) where the humidity was maintained at less than 10 ppm $H_2O$. A four electrode system was used in the SECM: two Li metal electrodes as the reference and counter, a Pt probe with a 10 μm diameter as the working electrode 1, and a $LiCoO_2$ substrate with a 3.22 mm radius as the working electrode 2. Before the experiment, the Pt probe was polished using a diamond slurry (15 μm BASI) and the substrate was dried under vacuum at 80°C for 12 hrs. The probe was scanned at 3.0 μm $s^{-1}$ in the PAC experiments. The potential of the non-scanning probe was swept from 3.8 to 4.4 V with a scan rate of 5 mV $s^{-1}$ in the LSV experiments. All potentials in this study were referenced to the $Li/Li^+$ reference electrode.

## 3. RESULTS AND DISCUSSION

### *3.1 PACs above the $LiCoO_2$ substrate*

The distribution and transport of electrolyte components above the $LiCoO_2$ substrate can be investigated by carrying out PAC experiments [10]. To conduct the PAC experiments, the redox potentials of electrolyte components should be assigned. There are various components in the electrolyte used in this study including EC, DEC, $PF_6^-$ ions, $Li^+$ ions, and many of their solvated forms [11]. Among these electrolyte components, $PF_6^-$ can be more easily oxidized than the other components because it has the highest occupied molecular orbital (HOMO) energy value [12]. The oxidation potential of the electrolyte composed of 1.0 M $LiPF_6$ and EC/DEC (= 3/7) is also reported to be initiated at about 3.9 V (vs. Li/$Li^+$) due to the oxidation of $PF_6^-$ [13]. According to these previous studies, the probe potential was held at 4.8 V, which is sufficient for $PF_6^-$ ions to be oxidized in 1.0 M $LiPF_6$ EC/DEC (= 3/7). Furthermore, a potential was not applied to the $LiCoO_2$ substrate in the PAC experiments. When the probe is located far from the substrate, the steady-state current is recorded at the probe, as shown in Fig. 1.

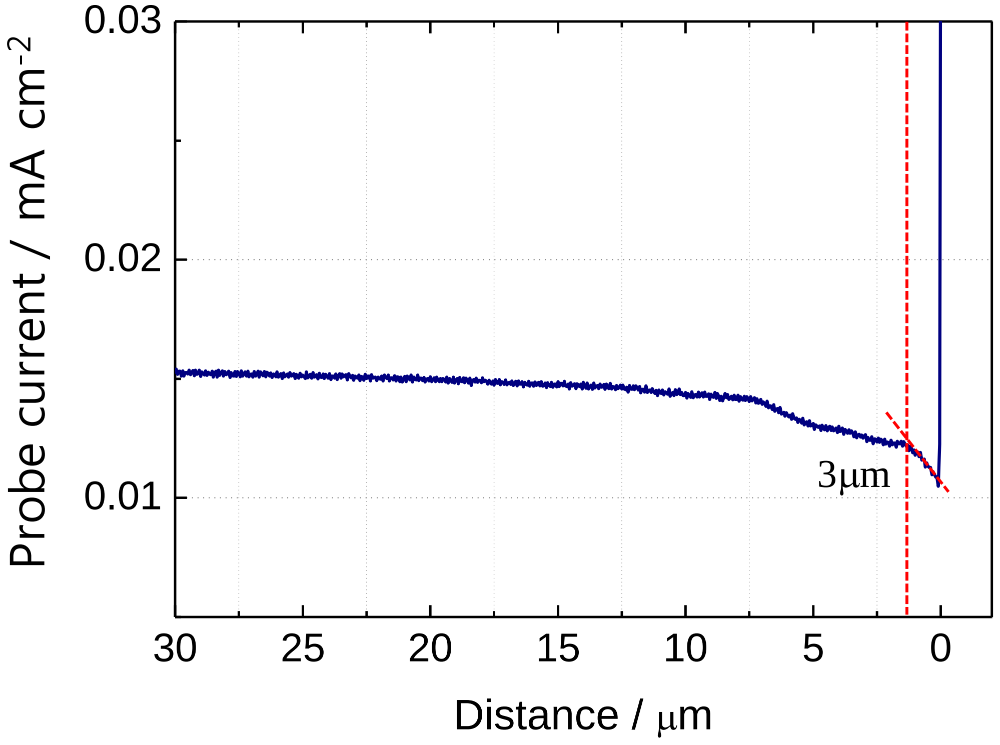


**Figure 1.** Probe scan curve obtained using the Pt probe above the $LiCoO_2$ substrate in 1.0 M $LiPF_6$ EC:DEC (=3:7). The probe was scanned at 3 μm $s^{-1}$.

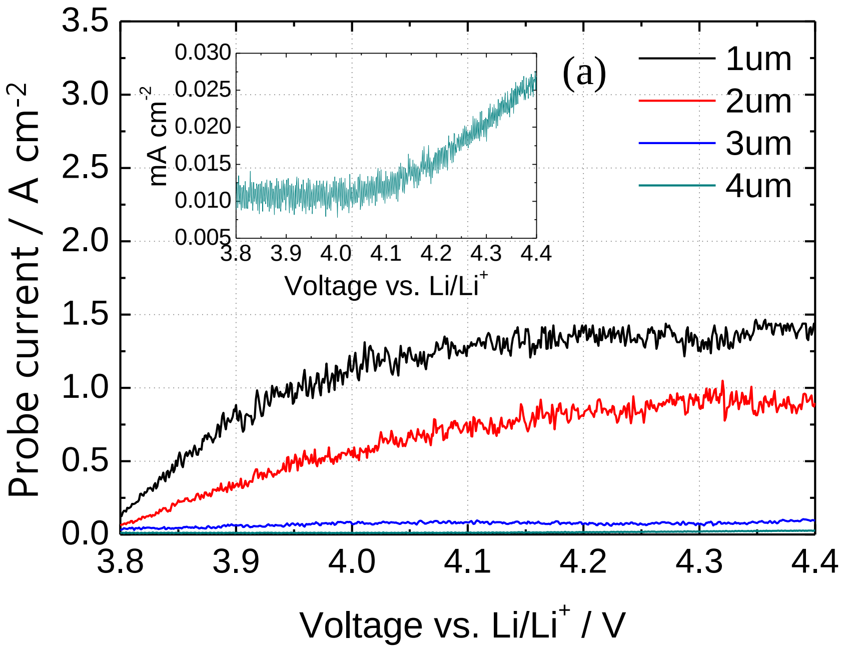
This result is in agreement with the theoretical steady-state current ($i_{T,\infty}$) determined by the following equation, which is mainly dependent on the concentration of electrolyte in the bulk electrolyte [14].

$$i_{T,\infty}=4nFDCa \quad (1)$$

In this equation, $n$ is the number of electrons transferred during the redox reaction, $F$ is the Faraday constant, $D$ is the diffusion coefficient of the redox species, $C$ is the bulk concentration, and $a$ is the radius of the probe. The probe current gradually decreases as it apporaches the substrate from a position of about 8 μm. This phenomenon is similar to the negative feedback behavior above the insulating substrate and is generated when the transport of the electrolyte is disturbed by the insulator [15, 16]. As shown in Fig. 1, however, the curve is not typical of negative feedback behavior. That is, the probe current increases abruptly when the Pt probe nearly contacts the substrate. This means that the $LiCoO_2$ substrate is not a simple insulator and changes to a high conductor when the probe at 4.8 V nearly contacts it. The question remains as to what makes the probe current increase at the contacting point. Previously, we investigated the electrolyte transport above the $LiCoO_2$ substrate over 4.0 V by the PAC method [10]. In that case, the probe current dramatically increased at about 30 μm above the same $LiCoO_2$ substrate, showing typical positive feedback behavior. This phenomenon was analyzed and it was found that the $Li^+$ ions deintercalating from $LiCoO_2$ substrate participated in supermolecules intensively near the $LiCoO_2$ substrate. As in the preceding study, it is concluded that the probe current increases abruptly near the contact point at the substrate because the concentration of the oxidant, $PF_6^-$ ions, is increased or the probe is contacted with the substrate completely.

### *3.2 LSV above the $LiCoO_2$ substrate*

A LSV experiment with the probe over the $LiCoO_2$ substrate was conductued to verify the mechanism for the increased current when the Pt probe nearly contacted the substrate.



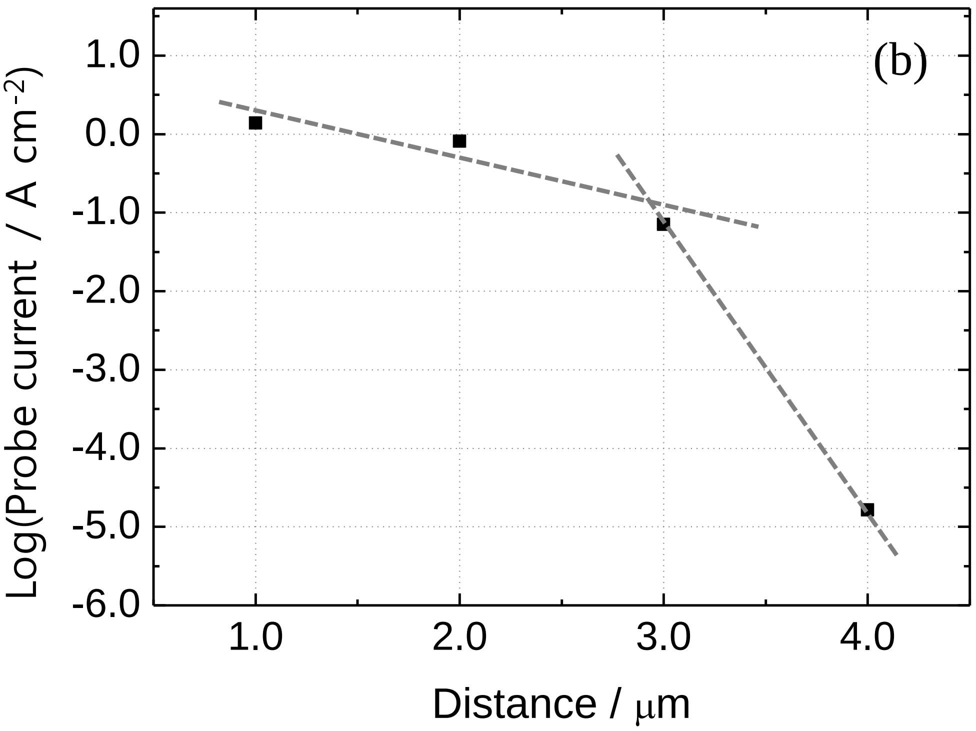


**Figure 2.** (a) Linear sweep voltammetry with the Pt probe from 3.8 to 4.4 V above the $LiCoO_2$ substrate as a function of distance and (b) a logarithm plot of the probe current collected at 4.2 V.

In this experiment, the LSV was measured at four fixed positions (4, 3, 2, 1 μm) and the probe potential was swept from 3.8 to 4.4 V above the substrate where no potential was applied. The experiments were designed to extend the electrochemical reaction time at the probe which can magnify the electrochemical reaction. Contrary to the current behaviors obtained from the PAC method, the currents of the LSV increased as the probe approached the substrate within a distance of 3 μm, as shown in Fig. 2(a). To obtain the general tendency, the current at 4.2 V was plotted as the *log*(probe current) *vs.* distance in Fig. 2(b). The probe current significantly increased when the probe was positioned within 3 μm from the substrate. Namely, the current increased by a factor of 3,000 when the probe was moved from a distance of 4 to 3 μm away from the substrate. This result is contrary to the probe current obtained by the PAC which decreased significantly within a distance of 3 μm from the substrate, as shown in Fig. 1. Therefore, it is important to determine what causes the difference between the PAC and the LSV experiments.

In the case of the PAC experiments, the $PF_6^-$ ions could be fully supplied near the probe because the probe is continuously moving. This means that the probe current would be influenced by the bulk concentration of the oxidizable component ($PF_6^-$ ions) only around the probe. Therefore, the dramatic decrease of the probe current within 3 μm from the substrate could be interpreted to be due to the impeded influx of oxidizable $PF_6^-$ ions to the probe because of the narrow gap. However, as explained before, the probe current in the LSV experiments was significantly increased as the probe approached the substrate within the same 3 μm distance. These phenomena could be explained as $PF_6^-$

ions are supplied at a higher concentration even in the narrow gap between the substrate and the non-scanning probe in the LSV experiments. Physically, it becomes difficult not only for the $PF_6^-$ ions to flow into this narrow gap but also for the oxidized species, $PF_6^0$, to flow out from this gap. Moreover, the oxidized form is less stable than $PF_6^-$ in the electrolyte and its electrochemical reduction potential is shifted to a more positive level than the $PF_6^-$ ions. In such circumstances, the oxidized species would be more and more imprisoned near the $LiCoO_2$ substrate as the probe closely approaches the substrate. As a result, the oxidized form could be reduced to its original state, $PF_6^-$ ions, with the oxidation of the $LiCoO_2$ substrate. By this continuous process, the $Li^+$ ions would be simultaneously deintercalated from the $LiCoO_2$ particle ($LiCoO_2 \rightarrow Li_{1-x}CoO_2 + Li^+$) and take part in the new solvation structure.

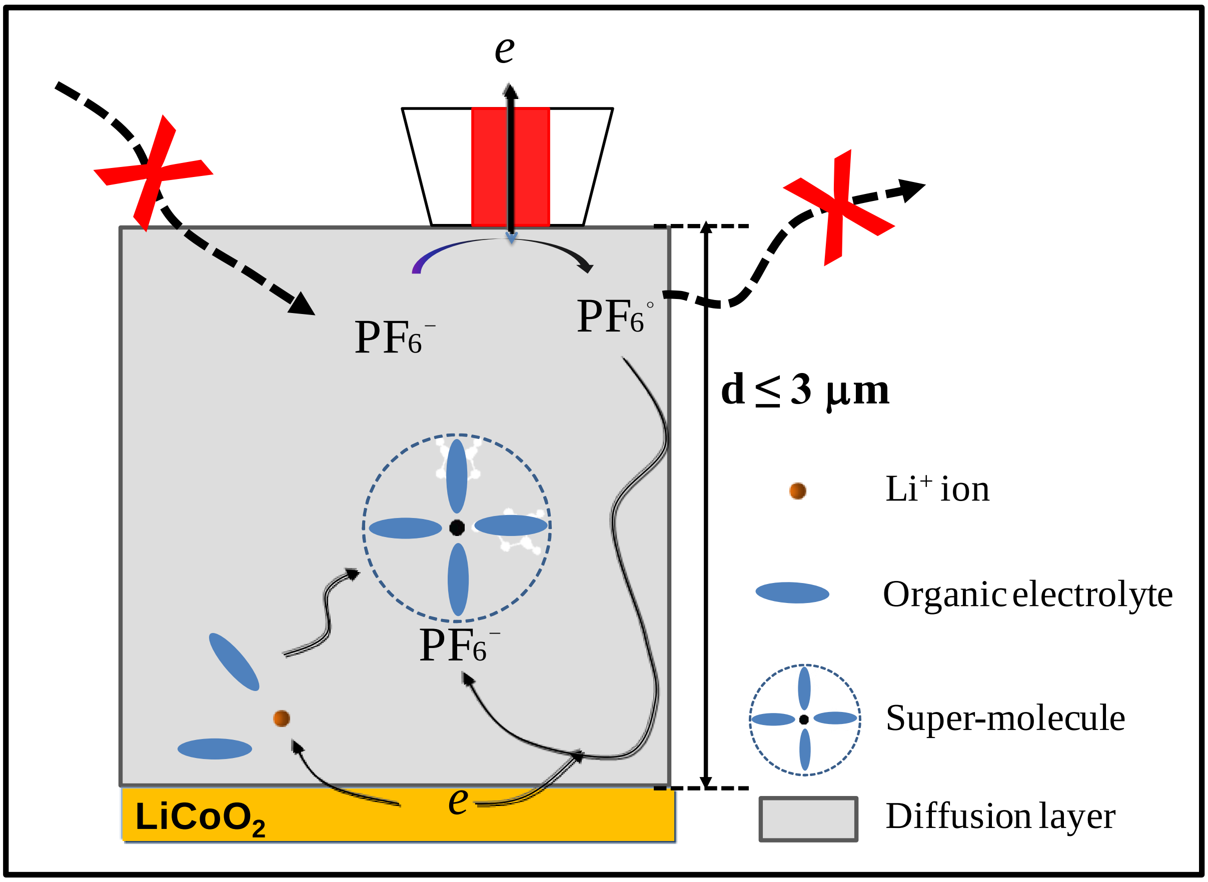


**Figure 3.** Schematic diagram of the redox reaction of $PF_6^-$ ions through the PG/SG→PC mode between the Pt probe and the $LiCoO_2$ substrate within a distance of 3 μm.

Fig. 3 shows a schematic diagram of these electrochemical reactions generated within this narrowed gap between the probe and the substrate.

Unlike the typical feedback mode in SECM experiments such as the SG/PC mode and the PG/SC mode, the flow of these electrochemical reactions could be referred to as the PG/SG→PC mode. This mode is composed of the oxidation of $PF_6^-$ ions at the probe, the diffusion of the oxidized species to the substrate, the reduction to $PF_6^-$ ions by the substrate and the dissociation of $Li^+$ ions from the substrate, and finally, recollection as an oxidation current at the probe. As this PG/SG→PC process results in the indirect oxidation of the $LiCoO_2$ substrate, which is more severe than the typical SG/PC mode, it is a new technology to design an electrolyte to result in high rate performance of Li ion batteries. Up to now, our group has intensively reported the importance of the electrolyte distribution at the electrode interface to upgrade the performance of Li ion batteries including the analysis of the initial absorbing behavior of Li ion batteries, electrochemical absorption effect of $BF_4$ anion salt on SEI layer formation, electrolyte optimization for Li ion batteries based on charge profile analysis, and enhancement of the $Li^+$ ion transfer reaction at the $LiCoO_2$ interface by 1,3,5-trifluorobenzene [17-20]. From all of these studies, we verified that the analysis method of the electrolyte transport above the substrate by a scanning/non-scanning probe provides a key technology tool to enhance the high rate performance of Li ion batteries.

## 4. CONCLUSIONS

We investigated electrolyte transport above the $LiCoO_2$ substrate using the PAC and LSV of SECM. The PAC data showed typical negative feedback curves above the substrate with no applied potential. At very close distances to the substrate, however, the probe current increased, which is different than the typical negative curve. In the case of the LSV experiment with the distance from the substrate, meanwhile, the probe current increased by a factor of 3,000 when the probe was moved from 4 to 3 μm from the substrate. This difference was induced by the redox reaction of $PF_6^-$ ions accumulated in the narrow space between the substrate and the probe, which were oxidized by the probe and reduced by $LiCoO_2$ particles, rotationally. This can be referred to as the PG/SG→PC mode and is a promising tool to analyze electrolyte transport above the substrate and the oxidation ability of $LiCoO_2$ substrates to result in a high rate performance of Li ion batteries.

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## References

1. Y. Sato, K. Nagayama and T. Takamura, *Journal of Power Sources,* 189 (2009) 490-493.
2. S. Patoux, L. Daniel, C. Bourbon, H. Lignier, C. Pagano, F. Le Cras, S. Jouanneau and S. Martinet, *Journal of Power Sources*, 189 (2009) 344-352.
3. I.Thorat, V. Mathur, J. Harb and D. Wheeler, *Journal of Power Sources*, 162 (2006) 673-678.
4. T. Takamura, K. Endo, L. Fu, Y. Wu, K. Lee and T. Matsumoto, *Electrochimica Acta*, 53 (2007) 1055-1061.
5. K. Smith and C. Wang, *Journal of Power Sources*, 160 (2006) 662-673.
6. F. Millange, R. Walton and D. O'Hare, *Journal of Materials Chemistry*, 10 (2000) 1713-1720.
7. Y. Cohen and D. Aurbach, *Electrochemistry Communications*, 6 (2004) 536-542.

8. R. Martin and P. Unwin, *Anal. Chem*, 70 (1998) 276-284.
9. J. Fernandez and A. Bard, *Anal. Chem*, 76 (2004) 2281-2289.
10. F. Xu, B. Beak and C. Jung, *J. Solid State Electrochem. Online published* (DOI 10.1007/s10008-011-1325-8)
11. Y. Wang, S. Nakamura, M. Ue and P. Balbuena, *J. Am. Chem. Soc*, 123 (2001) 11708-11718.
12. P. Johansson, *J. Phys. Chem*. A, 110 (2006) 12077-12080.
13. M. Egashira, H. Takahashi, S. Okada and J. Yamaki, *Journal of Power Sources*, 92 (2001) 267-271.
14. R. Tel-Vered and A. Bard, *J. Phys. Chem*. B, 110 (2006) 25279-25287.
15. P. Unwin and A. Bard, The *Journal of Physical Chemistry*, 95 (1991) 7814-7824.
16. O. Fontaine, C. Lagrost, J. Ghilane, P. Martin, G. Trippe, C. Fave, J. Lacroix, P. Hapiot and H. Randriamahazaka, *Journal of Electroanalytical Chemistry*, 632 (2009) 88-96.
17. C. Jung, *Solid State Ionics*, 179 (2008) 1717-1720.
18. M. Cha and C. Jung, *Journal of applied electrochemistry*, 39 (2009) 955-960.
19. B. Baek and C. Jung, *Electrochimica Acta*, 55 (2010) 3307-3311.
20. C. Jung and D.W. Lee, *Journal of the Korean Vacuum Society* 16 (2007) 227